

\*  
\* W E L C O M E T O T H E \*  
\* U. S. P A T E N T T E X T F I L E \*  
\* \*

=> s (polyester# or copolyester#) and manganese and cobalt? and  
titanium and (phosphorous or phosphoric or phosphinic) (w)acid#

115211 POLYESTER#

5337 COPOLYESTER#

46360 MANGANESE

62553 COBALT?

98471 TITANIUM

25495 PHOSPHOROUS

66635 PHOSPHORIC

1969 PHOSPHINIC

379266 ACID#

58808 (PHOSPHOROUS OR PHOSPHORIC OR PHOSPHINIC) (W)ACID#

L1 582 (POLYESTER# OR COPOLYESTER#) AND MANGANESE AND  
COBALT? AND

TIT

ANIUM AND (PHOSPHOROUS OR PHOSPHORIC OR  
PHOSPHINIC) (W)ACID#

=> s 11 and optical(w)brightener#

215149 OPTICAL

7509 BRIGHTENER#

3979 OPTICAL(W)BRIGHTENER#

L2 3 L1 AND OPTICAL(W)BRIGHTENER#

=> s 11 not 12

L3 579 L1 NOT L2

=> s 13 and color?

267383 COLOR?

L4 345 L3 AND COLOR?

=> s 13 not 14

L5 234 L3 NOT L4

=> d 12 1-3 ab cit

US PAT NO: 5,324,574 [IMAGE AVAILABLE]

L2: 1 of 3

#### ABSTRACT:

A novel biaxially stretched \*\*polyester\*\* film having excellent transparency and slipperiness is disclosed. The biaxially stretched

\*\*polyester\*\* comprises a \*\*polyester\*\* composition which exhibits a film

haze of not more than 1% after it is made into a film having a

thickness  
of 100 .mu.m and 50-500 ppm on the basis of the weight of  
monodispersed  
cross-linked high polymer particles having an average particle  
diameter  
of 0.8-1.4 .mu.m and exhibits a deformability of 1.2-5.0 in a  
biaxially  
stretched \*\*polyester\*\* film.

1. 5,324,574, Jun. 28, 1994, Biaxially stretched \*\*polyester\*\*  
film;  
Seiji Sakamoto, et al., 428/220, 327, 480, 483 [IMAGE AVAILABLE]

US PAT NO: 5,151,494 [IMAGE AVAILABLE]

L2: 2 of 3

**ABSTRACT:**

The invention is a \*\*polyester\*\* and a method for producing a  
\*\*polyester\*\* filament which has a combination of flame  
resistance and  
low pilling properties. The method comprises forming a  
\*\*polyester\*\*  
polymer from a mixture consisting essentially of terephthalate  
acid or  
dimethyl terephthalate, ethylene glycol, a chain branching agent  
having a  
functionalities of at least 3 and a \*\*phosphinic\*\* \*\*acid\*\* in the  
amount  
between 0.5 and 20 mole percent of the terephthalate acid and  
monomer. In  
particular, the invention also comprises the enhanced fiber  
formed by the  
process, as well as the fabrics having a pilling of about 3 to  
less than  
5 as measured in accordance with ASTM D-3512-82.

2. 5,151,494, Sep. 29, 1992, Flame resistant, low pilling  
\*\*polyester\*\*  
fiber; Jerry T. Munday, et al., 528/287; 524/116, 117, 120, 133,  
135, 708  
[IMAGE AVAILABLE]

US PAT NO: 5,145,941 [IMAGE AVAILABLE]

L2: 3 of 3

**ABSTRACT:**

The invention is a \*\*polyester\*\* and a method for producing a  
\*\*polyester\*\* fiber which has a combination of flame resistance  
and low  
pilling properties. The method comprises forming a \*\*polyester\*\*  
fiber  
made from a blend of two \*\*polyester\*\* polymers, one  
\*\*polyester\*\*  
polymer containing an oxysilicon compound and the second  
\*\*polyester\*\*  
polymer containing pentaerythritol and a \*\*phosphinic\*\* \*\*acid\*\*

in the amount between 0.5 and 20 mole percent of the terephthalate acid and monomer. In particular, the invention also comprises the enhanced fiber formed by the process, as well as the fabrics having a pilling of about 3 to less than 5 as measured in accordance with ASTM D-3512-82.

3. 5,145,941, Sep. 8, 1992, Flame resistant, low pilling  
\*\*polyester\*\*  
fiber; Jerry T. Munday, et al., 528/287; 524/116, 117, 120, 133,  
135,  
708; 525/444; 528/288 [IMAGE AVAILABLE]

=> d 14 1-100 ab cit.

=> d 15 1-100 ab cit

=> d 14 30 48 61 93 151 157 158 165 198 208 215 216 218 226 237  
238 270 290 294 301 324 ab cit

US PAT NO: 5,385,773 [IMAGE AVAILABLE] L4: 30 of  
345

ABSTRACT:

Disclosed is a process for producing \*\*copolymers\*\* having repeat units from a dicarboxylic acid component comprising at least 90 mol % terephthalic acid and a glycol component comprising about 10-95 mol % 1,4-cyclo-hexanedimethanol and from about 90-5 mol % ethylene glycol comprising reacting the dicarboxylic acid component and the glycol component at temperatures sufficient to effect esterification or transesterification and polycondensing the reaction product in the presence of a catalyst and inhibitor system consisting essentially of Mn, Zn, Ti, Ge and P, all parts by weight based on the weight of the \*\*copolymer\*\*.

30. 5,385,773, Jan. 31, 1995, \*\*Copolyester\*\* of cyclohexanenedimethanol and process for producing such \*\*polyester\*\*; Cheuk C. Yau, et al., 428/221, 174; 524/115, 431, 432, 440, 706, 779, 783, 785; 528/272, 277, 279, 280, 281, 283, 286, 307, 308.6 [IMAGE AVAILABLE]

US PAT NO: 5,340,907 [IMAGE AVAILABLE] L4: 48 of

**ABSTRACT:**

Disclosed is a process for producing \*\*copolymers\*\* having repeat units from a dicarboxylic acid component comprising at least 90 mol % terephthalic acid and a glycol component comprising about 10-95 mol % 1,4-cyclohexanedimethanol and from about 90-5 mol % ethylene glycol comprising reacting the dicarboxylic acid component and the glycol component at temperatures sufficient to effect esterification or transesterification and polycondensing the reaction product in the presence of a catalyst and inhibitor system consisting essentially of Mn, Zn, Ti, Ge and P, all parts by weight based on the weight of the \*\*copolymer\*\*.

48. 5,340,907, Aug. 23, 1994, \*\*Copolyester\*\* of cyclohexanedimethanol and process for producing such \*\*polyester\*\*; Cheuk C. Yau, et al., 528/274; 428/98; 528/272, 279, 280, 281, 286 [IMAGE AVAILABLE]

US PAT NO: 5,286,836 [IMAGE AVAILABLE]

L4: 61 of

345

**ABSTRACT:**

A process for forming \*\*polyesters\*\* that comprises the steps of esterifying a terephthalic acid and an ethylene glycol to produce an esterification product containing a bis (betahydroxyethyl) terephthalate, and continuously polycondensing the obtained esterification product to form a \*\*polyester\*\*. In both the esterifying step and the polycondensing step, a reaction catalyst consisting of a compound of antimony and a compound of \*\*titanium\*\* is used. The weight ratio of the compound of antimony to the compound of \*\*titanium\*\* is 0.01 to 100. The process of the present invention can considerably reduce both the esterification time and the polycondensation time and provides good \*\*color\*\*, reduced diethylene glycol content and reduced condensation of terminal carboxyl groups in the resulting \*\*polyesters\*\*.

61. 5,286,836, Feb. 15, 1994, Process for forming

\*\*polyesters\*\*; Sang  
S. Park, et al., 528/275, 272, 279, 285 [IMAGE AVAILABLE]

US PAT NO: 5,185,426 [IMAGE AVAILABLE]  
345

L4: 93 of

ABSTRACT:

A continuous direct esterification and polycondensation process is disclosed for the production of \*\*polyester\*\* comprising units of ethylene terephthalate as the major repeating units by supplying a slurry of mainly terephthalic acid and ethylene glycol to bis(betahydroxyethyl) terephthalate or its oligomer so as to carry out esterification, followed by polycondensation whereby the resulting oligomer is kept under increasingly reduced pressure, characterized in that a stabilizing solution of an aliphatic diol containing a diethyl or tributyl phosphite and a hindered phenolic phosphonate is added to the reaction mixture before the start of the polycondensation.

93. 5,185,426, Feb. 9, 1993, Process for the production of \*\*polyester\*\* with enhanced thermo-oxidative stability; Johannes M. Verheijen, et al., 528/272; 524/128, 539, 605, 710; 525/437, 444; 528/287, 308.6 [IMAGE AVAILABLE]

US PAT NO: 4,931,538 [IMAGE AVAILABLE]  
345

L4: 151 of

ABSTRACT:

The present invention relates to a polyethylene terephthalate based \*\*copolyester\*\* modified by aliphatic dicarboxylic acid containing not less than 9 carbon atoms and poly(tetramethylene oxide)glycol, and to a \*\*polyester\*\* resin composition comprising said \*\*copolyester\*\*. Said \*\*polyester\*\* resin composition exhibits excellent toughness, impact strength and moldability without harming the inherent characteristics of polyethylene terephthalate.

151. 4,931,538, Jun. 5, 1990, \*\*Copolyester\*\* and \*\*polyester\*\* resin composition comprising said \*\*copolyester\*\*; Murata Yoshifumi, et al.,

528/272, 295.3, 300, 302, 303, 304, 308, 308.3, 308.6 [IMAGE AVAILABLE]

US PAT NO: 4,820,795 [IMAGE AVAILABLE]  
345

L4: 157 of

ABSTRACT:

Disclosed is a \*\*polyester\*\* vessel having mouth, side wall and bottom portions formed of a \*\*polyester\*\* composed mainly of ethylene terephthalate units, wherein the thermoplastic \*\*polyester\*\* is a \*\*polyester\*\* containing a catalyst residue in an amount smaller than 1000 ppm as the metal, and in the thermoplastic \*\*polyester\*\* constituting the bottom portion of the vessel, the ratio of the thermal crystallization degree represented by the following formula:

100.times.(Q.<sub>sub.DC</sub> - Q.<sub>sub.AC</sub>)/Q.<sub>sub.DC</sub> (1)  
wherein Q.<sub>sub.AC</sub> stands for the heat quantity of crystallization at elevation of the temperature and Q.<sub>sub.DC</sub> stands for the heat quantity of crystallization at lowering of the temperature, is lower than 90%.

157. 4,820,795, Apr. 11, 1989, \*\*Polyester\*\* vessel and package; Sadao Hirata, et al., 528/272; 426/106, 113, 118; 528/274, 285, 308.3 [IMAGE AVAILABLE]

US PAT NO: 4,818,808 [IMAGE AVAILABLE]  
345

L4: 158 of

ABSTRACT:

A process for producing a linear \*\*polyester\*\* comprising a main structural unit of an aromatic dicarboxylic acid ester of an alkylene glycol, particularly, comprising a polyethylene terephthalate or polytetramethylene terephthalate unit, is provided. In the process of the invention, the polycondensation reaction is conducted in the presence of a niobic acid catalyst that is obtained by heat-treating a hydrated niobium compound at the temperature range between 80.degree. C. and 400.degree. C. The process of the invention is also effectively applied to the manufacture of an elastomeric \*\*polyester\*\* comprising a polyalkylene terephthalate as a hard segment and a polyalkylene glycol as a soft segment.

158. 4,818,808, Apr. 4, 1989, Process for producing  
\*\*polyesters\*\* using  
a niobium compound as a catalyst; Toshihiro Kushimoto, et al.,  
528/275;  
524/700, 706, 783, 784, 796; 528/277, 279, 283, 286, 308, 308.6  
[IMAGE  
AVAILABLE]

US PAT NO: RE 32,765 [IMAGE AVAILABLE] L4: 165 of  
345

ABSTRACT:

A \*\*polyester\*\* which when made into an article such as films, containers, bottles and the like has a very high clarity, a low haze value, and a neutral hue. In the preparation of the resin, an antimony catalyst is utilized along with small amounts of a bluing agent such as a \*\*cobalt\*\* compound and a phosphate compound with the phosphate compound generally being slightly in excess of an equivalent amount of the \*\*cobalt\*\* compound. The \*\*polyester\*\* is made from dicarboxylic acids and preferably aromatic acids such as terephthalic acid reacted with polyhydric alcohols.

165. RE 32,765, Oct. 11, 1988, High clarity \*\*colorless\*\*  
\*\*polyesters\*\*; Douglas D. Callander, et al., 524/382; 523/100;  
524/140,  
141, 398, 417, 605 [IMAGE AVAILABLE]

US PAT NO: 4,604,453 [IMAGE AVAILABLE] L4: 198 of  
345

ABSTRACT:

A \*\*polyester\*\* having an initial accumulation electric charge of not less than  $2.9 \mu C/mm.^2$  when determined in a melt state according to the method as hereinabove defined and a heat resistance of not more than 0.210 when determined according to the method as hereinabove defined, which comprises at least one magnesium compound and at least one phosphorus compound solubilized therein in amounts as satisfying the following formulas:

$$30.1 \leq \text{req.} [\text{Mg}] \leq 400 \quad (1)$$

$$0.8 \leq \text{req.} \text{Mg/P} \leq 3 \quad (2)$$

wherein [Mg] is the content (ppm) of the magnesium compound in terms of magnesium atom to the \*\*polyester\*\* and Mg/P is the atomic ratio of the magnesium atom in the magnesium compound to the phosphorus atom in the phosphorus compound.

198. 4,604,453, Aug. 5, 1986, \*\*Polyester\*\* composition; Katsuaki Kuze, et al., 528/481, 275, 276, 279, 280, 286 [IMAGE AVAILABLE]

US PAT NO: 4,535,118 [IMAGE AVAILABLE]  
345

L4: 208 of

**ABSTRACT:**

This invention discloses a high clarity, low haze \*\*polyester\*\* having improved heat-up rates which contains a very small amount of an infrared absorbent material, such as carbon black. This \*\*polyester\*\* is very useful as a material for making preforms for trays, containers, and the like. It is especially useful as a material from which beverage bottles can be made.

208. 4,535,118, Aug. 13, 1985, High clarity, low haze \*\*polyesters\*\* having reduced infrared heat-up times; Brian W. Pengilly, 524/398, 399, 417, 435, 496, 605 [IMAGE AVAILABLE]

US PAT NO: 4,501,878 [IMAGE AVAILABLE]  
345

L4: 215 of

**ABSTRACT:**

Disclosed is an improved process for the preparation of high molecular weight linear \*\*polyesters\*\*. In the preparation of \*\*polyesters\*\* by formation of a bis-dihydroxy ester prepolymer by transesterifying dimethyl terephthalate with a glycol in the presence of a catalyst followed by polycondensing the prepolymer in the presence of certain phosphorous-containing compounds and a transition metal-containing catalyst which remains active in the presence of said phosphorous compound, an improved rate of polycondensation is achieved by introducing the phosphorous compounds after first polycondensing the prepolymer to a

low molecular weight linear \*\*polyester\*\* having an average degree of polymerization of about 2 to about 10. The improved process further requires that the catalyst employed in the formation of the prepolymer be substantially inactive in the presence of said phosphorous compounds.

215. 4,501,878, Feb. 26, 1985, Process for the preparation of high molecular weight \*\*polyesters\*\*; L. Jane Adams, 528/286, 274, 277, 278, 280, 281, 283, 285 [IMAGE AVAILABLE]

US PAT NO: 4,499,226 [IMAGE AVAILABLE]

L4: 216 of

345

**ABSTRACT:**

A \*\*polyester\*\* which when made into an article such as films, containers, bottles and the like has a very high clarity, a low haze value, and a neutral hue. In the preparation of the resin, an antimony catalyst is utilized along with small amounts of a bluing agent such as a \*\*cobalt\*\* compound and a phosphate compound with the phosphate compound generally being slightly in excess of an equivalent amount of the \*\*cobalt\*\* compound. The \*\*polyester\*\* is made from dicarboxylic acids and preferably aromatic acids such as terephthalic acid reacted with polyhydric alcohols.

216. 4,499,226, Feb. 12, 1985, High clarity \*\*colorless\*\* \*\*polyesters\*\*; Fred L. Massey, et al., 524/382; 523/100; 524/140, 141, 398, 417, 605 [IMAGE AVAILABLE]

US PAT NO: 4,476,272 [IMAGE AVAILABLE]

L4: 218 of

**ABSTRACT:**

A high clarity, low haze \*\*polyester\*\* having improved heat-up rates contain very small amounts of an infrared absorbent material therein such as carbon black. Such \*\*polyesters\*\* are used in preforms as for making trays, etc., and especially in molding operations such as in the blow molding of beverage bottles.

218. 4,476,272, Oct. 9, 1984, High clarity, low haze  
\*\*polyesters\*\*  
having reduced infrared heat-up times; Brian W. Pengilly,  
524/398, 417,  
435, 496, 605 [IMAGE AVAILABLE]

US PAT NO: 4,454,312 [IMAGE AVAILABLE]

L4: 226 of

345

ABSTRACT:

A biaxially stretched \*\*polyester\*\* film comprising a  
\*\*polyester\*\* and  
zirconium as an internal particle material, produced by  
polycondensation  
of terephthalic acid or its esterified derivative and alkylene  
glycol as  
the major essential monomeric components in the presence of a  
polycondensation catalyst, during which zirconium in the form of  
any  
compound thereof in an amount of 80 to 2500 ppm in terms of  
zirconium  
atom to the \*\*polyester\*\* as produced being introduced into the  
reaction  
system at a stage after the initiation of the reaction and before  
the  
intrinsic viscosity of the reaction mixture reaching 0.2, and  
subjecting  
the produced \*\*polyester\*\* to film forming.

226. 4,454,312, Jun. 12, 1984, Biaxially stretched \*\*polyester\*\*  
films;  
Katsuaki Kuze, et al., 528/275, 272, 274, 279, 283, 285, 286,  
308.1,  
308.2 [IMAGE AVAILABLE]

US PAT NO: 4,408,004 [IMAGE AVAILABLE]

L4: 237 of

345

ABSTRACT:

A high clarity, low haze \*\*polyester\*\* having improved heat-up  
rates  
contains very small amounts of an infrared absorbent material  
therein  
such as carbon black. Such \*\*polyesters\*\* are used in preforms as  
for  
making trays, etc., and especially in molding operations such as  
in the  
blow molding of beverage bottles.

237. 4,408,004, Oct. 4, 1983, High clarity, low haze  
\*\*polyesters\*\*  
having reduced infrared heat-up times; Brian W. Pengilly,  
524/398, 417,  
435, 496, 605 [IMAGE AVAILABLE]

US PAT NO: 4,401,804 [IMAGE AVAILABLE]  
345

L4: 238 of

ABSTRACT:

A process is provided for deactivation of catalyst residues in \*\*polyester\*\* compositions. The \*\*polyester\*\* compositions are provided by polymerizing diols and diacids, or mixtures of such diols and diacids, to form \*\*polyester\*\* compositions. The polymerization is carried out in the presence of a polymerization catalyst that leaves traces of such catalyst residues in the \*\*polyester\*\* composition. These catalyst residues can adversely affect the further processing and end use of the \*\*polyester\*\* composition. The present process provides deactivation of the catalyst residues by the use of a combination of a mono- or dihydrogen phosphonate or mono-, di-, or trihydrogen phosphate compound and a di- or triester phosphonate compound or a phosphite compound.

238. 4,401,804, Aug. 30, 1983, Deactivation of \*\*polyester\*\* catalyst residues; Willis C. Wooten, et al., 528/272, 480, 487 [IMAGE AVAILABLE]

US PAT NO: 4,208,527 [IMAGE AVAILABLE]  
345

L4: 270 of

ABSTRACT:

In a process for preparing high molecular weight poly-(ethylene terephthalate) in two stages, comprising, in the first stage, reacting a dialkyl ester of terephthalic acid with ethylene glycol in the presence of 35 to 290 ppm of \*\*manganese\*\*, in the form of a \*\*manganese\*\*-II salt effective as a catalyst, together with 6 to 95 ppm of \*\*cobalt\*\*, in the form of a \*\*cobalt\*\*-II salt effective as a catalyst, at a temperature of 170.degree. to 220.degree. C. to give a low molecular weight precondensate; then adding 45 to 140 ppm of phosphorus in the form of a phosphorus compound effective to minimize discoloration of the product poly-(ethylene terephthalate) due to said transesterification catalysts; and, in the second stage, effecting complete condensation of the

precondensate thus obtained, in the presence of catalysts at a temperature of 270.degree.-290.degree. C. and under low pressure, to give

high molecular weight poly-(ethylene terephthalate), an improvement is provided wherein, in the second stage, 115 to 230 ppm

of germanium, in the form of a germanium-IV salt effective as a catalyst, and 2 to <20 ppm of \*\*titanium\*\*, in the form of a \*\*titanium\*\*-IV salt effective as a catalyst, all quantity data for the

catalyst components being based on the weight parts of terephthalic acid

units, are added to the reaction mixture as the catalysts.

270. 4,208,527, Jun. 17, 1980, Process for the manufacture of high

molecular weight poly-(ethylene terephthalate); Gernot Horlbeck, et al., 528/279, 283, 286, 308.5 [IMAGE AVAILABLE]

US PAT NO: 4,131,601 [IMAGE AVAILABLE]

L4: 290 of

345

#### ABSTRACT:

A process for the preparation of substantially linear, highly polymerized

\*\*polyesters\*\* by polycondensing a glycol ester of an aromatic dicarboxylic acid and/or a low molecular weight condensate thereof, the

process being characterized by using as a polycondensation catalyst a

preformed titanate compound obtained by reacting a titanic acid ester

represented by the formula  $Ti(OR)_4$ , where R is an alkyl group having

from 1 to 5 carbon atoms, with an aromatic acid selected from the group

consisting of trimellitic acid, trimellitic anhydride, hemimellitic acid,

hemimellitic anhydride or a mixture of one or more thereof at a molar

ratio of from about 0.5 to about 2.5 mols of the aromatic acid per 1 mol

of the titanic acid ester, to thereby form \*\*polyesters\*\* which have a

high softening point and good \*\*color\*\* tone. SU

#### BACKGROUND OF THE INVENTION

##### 1. Field of the Invention

This invention relates to a process for the preparation of \*\*polyesters\*\*, in particular, to a process for the preparation of

substantially linear, highly polymerized aromatic \*\*polyesters\*\* having a high softening point and good \*\*color\*\* tone.

## 2. Description of the Prior Art

\*\*Polyesters\*\* obtained by reacting an aromatic dicarboxylic acid with a glycol have excellent mechanical, physical and chemical properties, and hence are widely used for fiber, film and other moulding materials. Among such \*\*polyesters\*\*, \*\*polyesters\*\* obtained by reacting an acid component consisting mainly of terephthalic acid with a glycol component selected from the group consisting of ethylene glycol, tetramethylene glycol, hexamethylene glycol and cyclohexane-1,4-dimethanol are especially important.

In manufacturing the aforesaid \*\*polyesters\*\*--e.g., polyethylene terephthalate, conventional processing consists of heating the ethylene glycol ester of terephthalic acid and/or a low molecular weight condensate thereof under reduced pressure to effect polycondensation. In carrying out the polycondensation reaction on a commercial scale, catalysts are used to accelerate reaction. The rate of polycondensation and the qualities of the resulting \*\*polyester\*\* are greatly influenced by the kind(s) of catalyst(s) used.

\*\*Titanium\*\* compounds are known as excellent catalysts for the above-described polycondensation reaction.

For example, U.S. Pat. No. 2,822,348, Haslam, issued Feb. 4, 1958, discloses tetraisopropyltitanate, and British patent specification No. 793,111 to I.C.I. Limited, published Apr. 9, 1958, discloses an organic titanate, such as tetramethyl titanate and tetrabutyl titanate as a catalyst in the polycondensation reaction.

Although \*\*titanium\*\* compounds result in a very rapid rate of polycondensation, they also result in the formation of \*\*polyesters\*\* having a distinctly yellow \*\*color\*\* and provide \*\*polyesters\*\* with a decreased softening point. Methods have also been proposed to avoid the

disadvantage of yellowness in \*\*polyesters\*\* formed as described.

For example, British Pat. No. 949,085 to I.C.I. Limited, published Feb.

12, 1964, discloses the use of a catalyst system which is the combination

of a germanium compound (such as germanium tetraethoxide) and a \*\*titanium\*\* compound (such as \*\*titanium\*\* tetraisopropoxide or \*\*titanium\*\* tetrabutoxide) whereby the disadvantage of yellowness in the

resulting \*\*polyester\*\* is considerably reduced. However, the rate of

Polycondensation is also reduced as compared to the use of a \*\*titanium\*\*

compound alone. Further, this catalyst system is difficult to store for

extended times because \*\*titanium\*\* compounds, such as \*\*titanium\*\*

tetraisopropoxide or \*\*titanium\*\* tetrabutoxide, easily lose catalytic

activity in the presence of a small amount of water.

British Pat. No. 851,061 to Goodyear Tire & Rubber Co., published Oct.

12, 1960, discloses the use of preformed organic titanate compounds

formed by the reaction of titanic acid esters with polyhydroxy compounds,

such as ethylene glycol or tetramethylene glycol, polycarboxylic compounds, such as maleic acid, phthalic acid and trimesic acid, or

hydroxy carboxylic compounds, such as lactic acid and hydroxy benzoic

acid. In the preparation of \*\*polyesters\*\*, these preformed organic

titanate compounds accelerate the rate of polymerization and permit the

formation of polymers of high molecular weight. However, as a result of

experiments performed by the present inventors, it was found that the

preformed organic titanate compounds disclosed in this British patent do

not fully overcome the disadvantage of yellowness of the obtained \*\*polyesters\*\* so as to provide a \*\*color\*\* tone suitable for commercial

use. In addition, for example, the preformed organic titanate compound

derived from phthalic acid does not sufficiently accelerate the rate of

Polymerization. Finally, it is difficult to uniformly react trimesic acid

(benzene-1,3,5-tricarboxylic acid) with a titanic acid ester.

## SUMMARY OF THE INVENTION

It has now been surprisingly found that if a preformed titanate compound obtained by reacting a titanic acid ester with an aromatic tricarboxylic acid having the capacity to form an anhydride is used as a catalyst in the polycondensation of an aromatic dicarboxylic acid with a glycol to form a \*\*polyester\*\*, the above-mentioned disadvantages of the prior art can be substantially overcome.

It is, therefore, one object of the present invention to provide a process for the preparation of substantially linear, highly polymerized \*\*polyesters\*\* having a high softening point and good \*\*color\*\* tone.

It is another object of the present invention to provide a process for the preparation of \*\*polyesters\*\* using a polycondensation catalyst which is easily obtained and storable for extended periods of time without degradation.

The above-mentioned objects are attained by the process for the preparation of \*\*polyesters\*\* in accordance with the present invention, which comprises polycondensing a glycol ester of an aromatic dicarboxylic acid and/or a low molecular weight condensate thereof while removing glycol therefrom in the presence of a polycondensation catalyst which is preformed titanate compound obtained by reacting a titanic acid ester represented by the formula  $Ti(OR)_4$ , where R is an alkyl group having from 1 to 5 carbon atoms, with an aromatic acid selected from the group consisting of trimellitic acid (benzene-1,2,4-tricarboxylic acid), trimellitic anhydride, hemimellitic acid (benzene-1,2,3-tricarboxylic acid), hemimellitic anhydride or a mixture of one or more thereof.

290. 4,131,601, Dec. 26, 1978, Process for the preparation of \*\*polyesters\*\*; Satoshi Hashimoto, et al., 528/279, 308 [IMAGE AVAILABLE]

US PAT NO: 4,115,371 [IMAGE AVAILABLE]  
345

L4: 294 of

ABSTRACT:

A process for the production of high molecular weight low \*\*color\*\* polyethylene terephthalates using a particulaarly effective polycondensation catalyst is disclosed. \*\*Titanium\*\* tetrabutylate is added to the reaction mixture after the initial esterification or transesterification reaction is about 95% complete and the polycondensation is completed at temperatures between about 200 and 270.degree. C under reduced pressure. Metaphosphoric acid or its alkali or alkaline earth metal salts are added with the \*\*titanium\*\* tertrabutylate to control the \*\*color\*\*. Commonly accepted catalysts may be employed for the initial esterification or transesterification. Polymers with intrinsic viscosities in excess of 0.7 dl/g and yellowness numbers less than 6 can be produced.

294. 4,115,371, Sep. 19, 1978, Stabilization of polycondensates of polyethylene terephthalate; Peter Bier, et al., 524/605; 528/275, 279,  
286 [IMAGE AVAILABLE]

US PAT NO: 4,096,122 [IMAGE AVAILABLE]  
345

L4: 301 of

ABSTRACT:

A process for producing a linear \*\*polyester\*\* which comprises:  
(1) condensing excess 1,4-butanediol with a lower alkyl ester of an aromatic dicarboxylic acid at a temperature of less than 200.degree. C;  
(2) removing uncondensed 1,4-butanediol therefrom so that the reaction mixture contains no more than 1% by weight 1,4-butanediol;  
(3) condensing the so-formed dicarboxylic acid-bis-(4-hydroxy butyl ester) and any oligomer thereof with a dicarboxylic acid at a temperature of 200 to 250.degree. C, the dicarboxylic acid being present in no more than a stoichiometric amount; and  
(4) polycondensing the resultant condensate by heating the same at between 250.degree. and 310.degree. C in a vacuum.

301. 4,096,122, Jun. 20, 1978, Process for the production of

\*\*polyesters\*\* of 1,4-butanediol; Gerhard Schade, et al.,  
528/278, 275,  
276, 280, 283, 286, 302, 304, 305 [IMAGE AVAILABLE]

US PAT NO: 3,951,886 [IMAGE AVAILABLE]

L4: 324 of

345

**ABSTRACT:**

A process for producing \*\*polyester\*\* resins, such as saturated \*\*polyester\*\* resin, alkyd resin and unsaturated \*\*polyester\*\* resin from \*\*polyester\*\* wastes, which comprises depolycondensing \*\*polyester\*\* wastes with at least one polyol in the presence of at least one titanyl oxalate compound and/or \*\*titanium\*\* tartrate compound and subsequently polycondensing the resulting depolycondensation product with at least one polycarboxylic acid or its anhydride or with at least one polycarboxylic acid or its anhydride and at least one polyol, optionally in the presence of at least one phosphorus compound.

324. 3,951,886, Apr. 20, 1976, Process for producing  
\*\*polyester\*\* resin; Hideo Miyake, et al., 521/48.5; 528/279; 560/80, 83, 89,  
120, 127,  
198 [IMAGE AVAILABLE]

=> d 15 22 36 ab cit

US PAT NO: 5,302,686 [IMAGE AVAILABLE]

L5: 22 of

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**ABSTRACT:**

A hollow article or sheet of a \*\*copolyester\*\* which comprises, as main components, terephthalic acid as a dicarboxylic acid component and ethylene glycol as a diol component and which is characterized by:  
(1) isophthalic acid as a dicarboxylic acid component being from 0.5 to 3.0 mol %,  
(2) diethylene glycol as a diol component being from 1.0 to 2.5 mol %,  
(3) the intrinsic viscosity being from 0.60 to 1.50 dl/g,  
(4) the concentration of terminal carboxyl groups being at most 18 eq/ton, and  
(5) the content of a cyclic trimer being at most 0.40% by weight.

22. 5,302,686, Apr. 12, 1994, Hollow container and stretched film made of a \*\*copolyester\*\*; Katsuji Tanaka, et al., 428/35.7; 264/209.1, 291, 294; 428/34.1; 528/272, 283, 285, 302, 305, 308.6, 481, 503 [IMAGE AVAILABLE]

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ABSTRACT:

A \*\*copolyester\*\* which comprises, as main components, terephthalic acid as a dicarboxylic acid component and ethylene glycol as a diol component and which is characterized by:  
(1) isophthalic acid as a dicarboxylic acid component being from 0.5 to 3.0 mol %,  
(2) diethylene glycol as a diol component being from 1.0 to 2.5 mol %,  
(3) the intrinsic viscosity being from 0.60 to 1.50 dl/g,  
(4) the concentration of terminal carboxyl groups being at most 18 eq/ton, and  
(5) the content of a cyclic trimer being at most 0.40% by weight.

36. 5,262,513, Nov. 16, 1993, \*\*Copolyester\*\*, and hollow container and stretched film made thereof; Katsuji Tanaka, et al., 528/272; 428/34.1, 364, 480; 528/283, 284, 302, 308, 308.6 [IMAGE AVAILABLE]

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